

Preparation of Transition Metal Sulfide Nanoparticles via Hydrothermal Route

(Penyediaan Zarah Sulfida Logam Peralihan Bersaiz Nano Melalui Kaedah Hidroterma)

FEI-LING PUA, CHIN-HUA CHIA, SARANI ZAKARIA*, TZE-KHONG LIEW,
MOHD AMBAR YARMO & NAY-MING HUANG

ABSTRACT

Nano sized copper sulfide, iron sulfide and molybdenum sulfide were successfully synthesised via a simple hydrothermal method. Sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \times 5\text{H}_2\text{O}$) and hydroxylamine sulfate ($(\text{H}_3\text{NO})_2 \times \text{H}_2\text{SO}_4$) were used as the starting materials and reacted with the transition metal source at 200°C for 90 min. The products were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX) and Fourier transform infrared spectroscopy (FTIR). Spherical shape CuS and FeS_2 nanoparticles with high crystallinity were successfully produced. The transmission electron micrographs revealed the well-dispersibility of the produced nanoparticles. Scanning electron micrograph showed the MoS_2 nanoparticles possessed a spherical shape with sheet-like structure covering on the outer surface of the particles.

Keywords: Electron microscopy; hydrothermal; nanomaterials; sulfide; transition metal

ABSTRAK

Kuprum sulfida, ferum (IV) sulfida dan molibdenum sulfida bersaiz nano telah berjaya disintesis melalui kaedah hidroterma. Natrium tiosulfat pentahidrat ($\text{Na}_2\text{S}_2\text{O}_3 \times 5\text{H}_2\text{O}$) dan hidrosilamina sulfat ($(\text{H}_3\text{NO})_2 \times \text{H}_2\text{SO}_4$) telah digunakan sebagai bahan pemula untuk bertindak balas dengan sumber logam peralihan pada suhu 200°C selama 90 minit. Produk akhir telah dicirikan dengan pembelauan sinar-X (XRD), mikroskopi elektron transmisi (TEM), mikroskopi elektron imbasan (SEM), analisis penyebaran tenaga sinar-X (EDX), dan spektrometer infra-merah transformasi Fourier (FTIR). Nanozarah CuS dan FeS_2 yang berbentuk sfera dan mempunyai darjah penghabluran yang tinggi berjaya dihasilkan. Mikrograf elektron transmisi menunjukkan taburan saiz nanozarah tersekat dengan baik. Mikrograf elektron imbasan menunjukkan bahawa nanozarah MoS_2 berbentuk sfera dengan permukaan luar zarah diliputi oleh struktur berbentuk kepingan.

Kata kunci: Hidroterma; logam peralihan; mikroskopi elektron; nanobahan; sulfida

INTRODUCTION

Catalysts have been widely used in past for a variety of reactions and processes due to their excellent physical and chemical properties. Recently, crystalline and partially crystalline nano-sulfides have been extensively studied due to their numerous potential applications as catalysts for coal liquefaction, solid lubricants, rechargeable batteries, solar cell devices, and coatings for microwave shields (Alejandra et al. 2008; Hu et al. 2002; Qin et al. 2005; Tian et al. 1995). Particles size plays an important role in determining the dispersivity and activity of the catalysts, and the optimum size ranges from 10 to 20 nm (Tian et al. 1995). Control over the size of sulfide particles is, therefore, of great importance.

To date, various techniques have been developed to synthesize transition metal sulfides, including mechanochemical (Baláz et al. 2003), thermal decomposition (Monteiro et al. 2001), microwave irradiation (Liao et al. 2001), sonochemical (Wang et al. 2002), and hydrothermal

processes (Zou et al. 2007). Among them, hydrothermal synthesis offers an attractive method due to its simplicity and productivity. In addition, under supercritical condition, it leads to the formation of nanoscale products, which cannot be obtained by classical routes (Subba et al. 2008).

In this study, we developed a hydrothermal route to prepare transition metal (Cu, Mo and Fe) sulfide nanoparticles in the presence of sodium thiosulfate and hydroxylamine sulfate. Hydroxylamine sulfate serves not only as the sulfur source but also a strong acid to create the acidic condition for the formation of nanoparticles.

EXPERIMENTAL

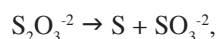
Sodium thiosulfate pentahydrate ($\text{Na}_2\text{S}_2\text{O}_3 \times 5\text{H}_2\text{O}$), hydroxylamine sulfate ($(\text{H}_3\text{NO})_2 \times \text{H}_2\text{SO}_4$), cupric sulfate pentahydrate ($\text{CuSO}_4 \times 5\text{H}_2\text{O}$), sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \times 2\text{H}_2\text{O}$), and ferrous chloride tetrahydrate ($\text{FeCl}_2 \times 4\text{H}_2\text{O}$) were used without further purification.

In a typical procedure, stoichiometric mixtures of the transition metal salt ($\text{CuSO}_4 \times 5\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \times 2\text{H}_2\text{O}$, or $\text{FeCl}_2 \times 4\text{H}_2\text{O}$), $\text{Na}_2\text{S}_2\text{O}_3 \times 5\text{H}_2\text{O}$, and $(\text{H}_3\text{NO})_2 \times \text{H}_2\text{SO}_4$ were dissolved in 60 mL of distilled water and loaded into a 60 mL stainless steel autoclave under stirring. The autoclave was sealed and heated to 200°C for 90 minutes and then allowed to naturally cool to room temperature. The resulting precipitate was washed with distilled water and methanol several times before being dried at 80°C for 24 hours.

X-ray diffraction (XRD) patterns were obtained using a Siemens D5000 diffractometer with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). The powders were scanned at a scanning rate of $0.02^\circ \text{ s}^{-1}$ between 2θ range of 20 and 80° . Transmission electron microscopy (TEM, Philips CM12) was employed to examine the size and dispersivity of the particles. The average particle size was measured from at least 50 particles from the TEM micrographs and the standard deviation was calculated. The morphology and elemental composition of the synthesized products were examined using a scanning electron microscope (SEM, Leo-1450 VP) and energy dispersive X-ray (EDX) spectroscopy, respectively. Fourier transform infrared studies of the samples were performed with a Perkin Elmer spectrometer.

RESULTS AND DISCUSSION

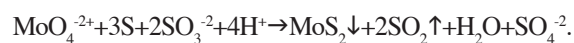
Figure 1a shows the X-ray diffraction pattern of the sulfide nanoparticles produced by mixing $\text{CuSO}_4 \times 5\text{H}_2\text{O}$ with $\text{Na}_2\text{S}_2\text{O}_3 \times 5\text{H}_2\text{O}$ and $(\text{H}_3\text{NO})_2 \times \text{H}_2\text{SO}_4$. This pattern confirmed the formation of a hexagonal covellite phase (CuS), which matches well with the standard XRD pattern (JCPDS Card File No. 06-0464; $a = 3.792 \text{ \AA}$, $b = 3.792 \text{ \AA}$ and $c = 16.34 \text{ \AA}$). No diffraction peaks relating to $\text{Cu}_{1.8}\text{S}$ and Cu_2S were observed, indicating purity of the obtained nanoparticles. Moreover, the sharp diffraction peaks reveal that well-crystallised sulfide nanoparticles can be produced through the hydrothermal process. The SEM (Figure 1b) and TEM (Figure 1c) images demonstrate the spherical shape and high-dispersivity of the resulting CuS nanoparticles. The estimated average particle size was $6.18 \pm 1.59 \text{ nm}$. In addition, EDX spectrum reveals the composition of the obtained particles to be CuS (Figure 1d), which agrees well with the XRD pattern. The infrared (IR) spectrum of the obtained CuS nanoparticles in Figure 1e shows the presence of small characteristic peaks at 1109 cm^{-1} , 1631 cm^{-1} , and 3400 cm^{-1} , corresponding to SO_4^{2-} and H_2O molecules. Acidic condition is not discussed although it have been mentioned as something important that will influence the formation of nanoparticles. The chemical reactions that led to the formation of CuS nanoparticles may be described by the following equations:



The XRD pattern of the iron sulfide nanoparticles produced is shown in Figure 2a. All of the diffraction peaks can be primarily indexed as cubic pyrite phase (FeS_2) with lattice constant $a = 5.42 \text{ \AA}$ (JCPDS Card No. 42-1340). The morphology of the particles is shown in Figure 2b. It is obvious that the particles are spherical-like in shape and tend to aggregate together. The average particle size was $4.32 \pm 0.76 \text{ nm}$ (Figure 2c). The EDX spectrum (Figure 2d) shows peaks of sulfur and iron elements, revealing the expected composition of FeS_2 . The FTIR spectrum of the FeS_2 nanoparticles shown in Figure 2e exhibited a broad peak centered around 3400 cm^{-1} and a band at 1635 cm^{-1} , which can be assigned to the O-H stretching and bending modes of water, respectively. In addition, the bands at 1130 cm^{-1} and 1070 cm^{-1} correspond to the asymmetric S-O stretching of the sulfate species while the peaks at 480 cm^{-1} and 600 cm^{-1} were consequence of the disulfides stretch (S-S) (Philiat & Marsan 1999). The presence of the sharp peaks at about 890 cm^{-1} and 798 cm^{-1} are attributed to the out-of-plane OH bending mode (Philip et al. 1995). Finally, the absorption near 2320 cm^{-1} may be due to N-H-O vibration (Kabil et al. 1996), suggesting organic contamination from the source materials. The formation of the FeS_2 can be described as follows:



The XRD pattern shown in Figure 3a exhibits the characteristic peaks of the rhombohedral phase molybdenite-3R, MoS_2 (JCPDS Card No. 17-0744; $a = 3.16 \text{ \AA}$, $b = 3.16 \text{ \AA}$ and $c = 18.33 \text{ \AA}$). The diffraction peaks are broad and weak, suggesting the nano-crystalline structure of the sulfide particles. This could be interpreted in terms of the requirement of further annealing on the as-prepared MoS_2 particles for improving the degree of crystallinity of the particles, as reported previously (Ma et al. 2008). The sulfide particles were uniform spheres that consisted of sheet like structure on the outer surface of the particles. This is consistent with the previous study on the preparation of MoS_2 particles using hydrothermal method (Ma et al. 2008). Figure 3c shows the TEM image of the resultant particles (Figure 3b). The particles were well-dispersed and the average particle size was about $10.66 \pm 2.31 \text{ nm}$. EDX analysis was also performed and the results (Figure 3d) indicated that the resultant particles were MoS_2 , which is consistent with the XRD patterns. Figure 3e shows the FTIR spectrum of the MoS_2 nanoparticles. The peaks appearing in this spectrum are generally similar to those in Figure 2(e). The possible chemical reaction involved can be expressed as follows:



We have demonstrated a viable hydrothermal method for synthesizing transition metal sulfide nanoparticles using sodium thiosulfate, hydroxylamine sulfate, and transition metal salts as source materials at 200°C for 90 minutes. By

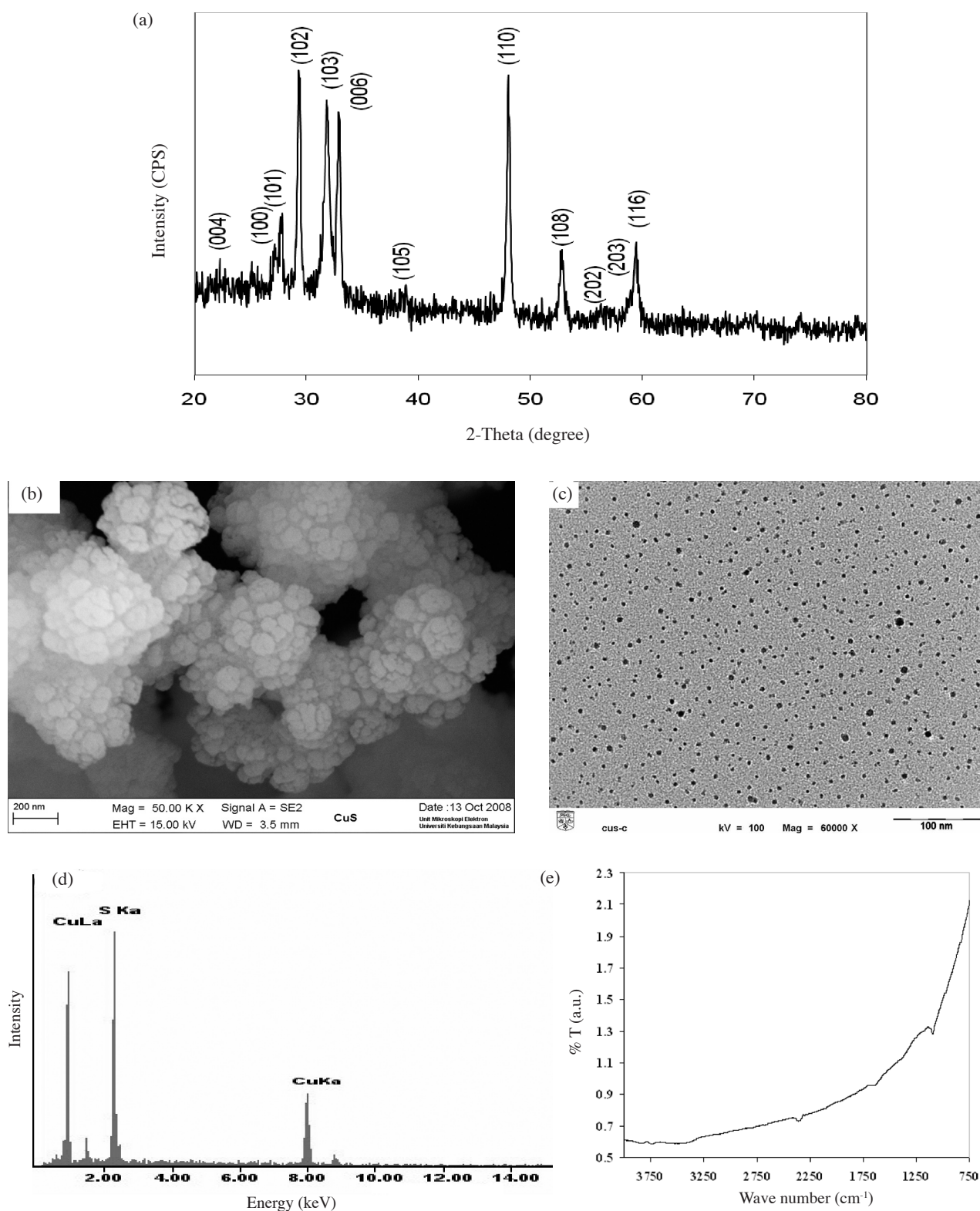


FIGURE 1. (a) XRD pattern of CuS nanoparticles with all of the peaks indexed for the hexagonal covellite phase (JCPDS card 06-0464) (b) SEM image of CuS nanoparticles; (c) TEM image of CuS nanoparticles; (d) EDX spectrum of CuS nanoparticles; (e) FTIR spectrum of the resultant CuS nanoparticles

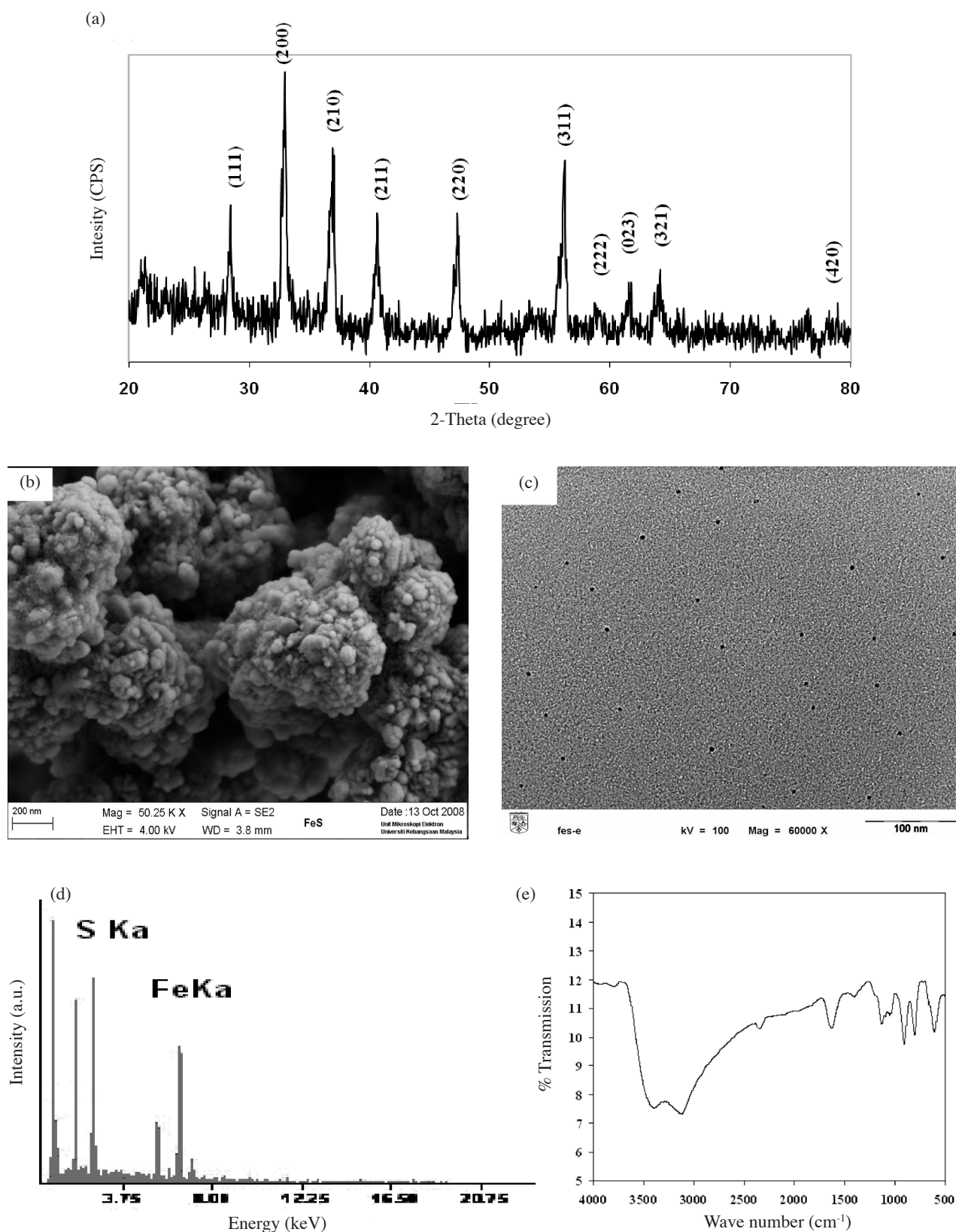


FIGURE 2. (a) XRD pattern of FeS_2 nanoparticles with all of the peaks indexed for the cubic pyrite FeS_2 (JCPDS card 42-1340); (b) SEM image of FeS_2 nanoparticles; (c) TEM image of FeS_2 nanoparticles; (d) EDX spectrum of FeS_2 nanoparticles; (e) FTIR spectrum of the resultant FeS_2 nanoparticles.

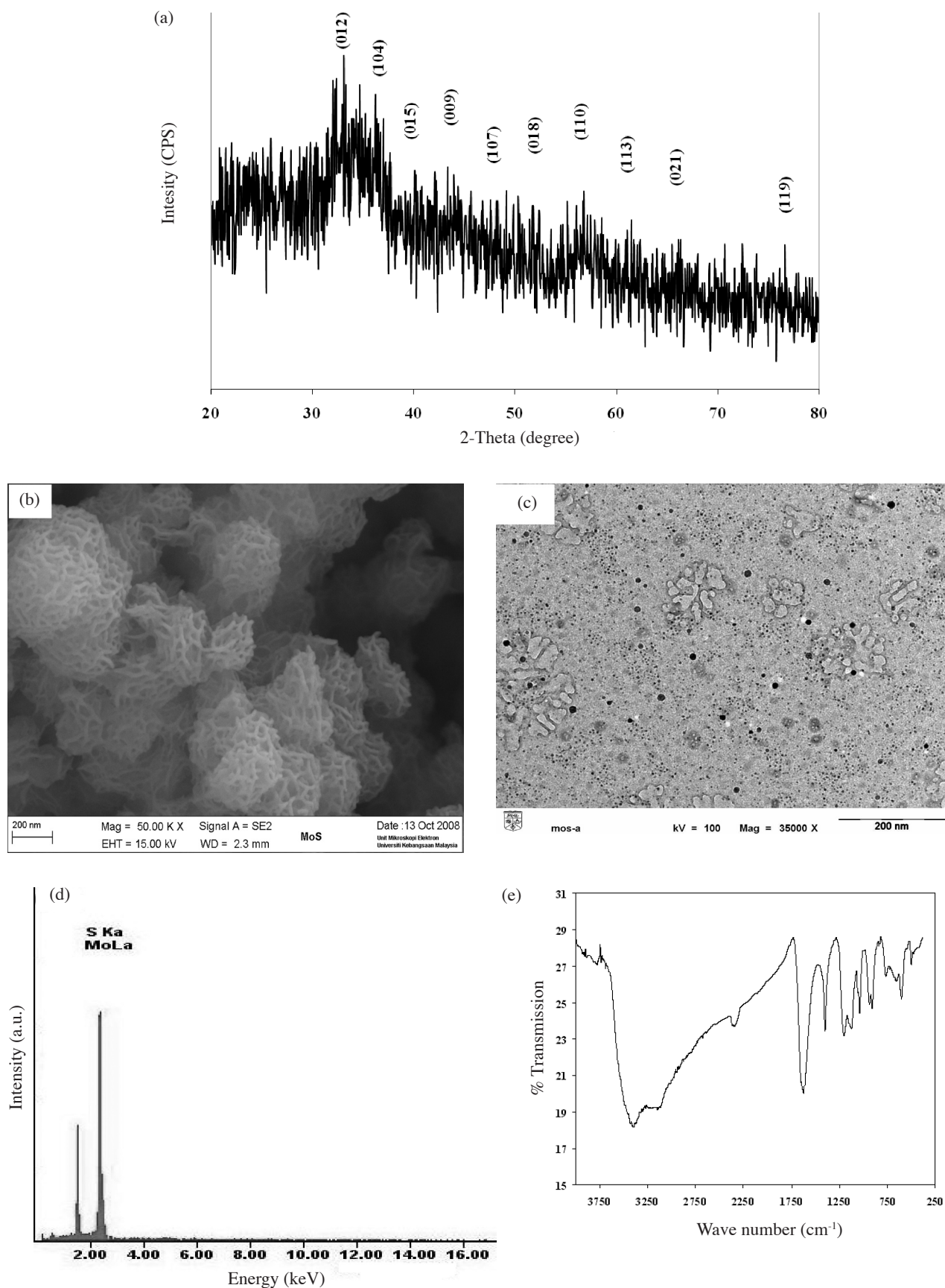


FIGURE 3. (a) XRD pattern of MoS_2 nanoparticles with all of the peaks indexed for the rhombohedral molybdenite-3R (JCPDS card 17-0744); (b) SEM image of MoS_2 nanoparticles observed; (c) TEM image of MoS_2 nanoparticles; (d) EDX spectrum of MoS_2 nanoparticles; (e) FTIR spectrum of the resultant MoS_2 nanoparticles

using this method, nano-sized hexagonal CuS, cubic FeS₂, and rhombohedral MoS₂ have been successfully produced. It is expected that this method can be used to synthesize sulfides for other transition metals, including Zn, Ni, Co, and Pb.

ACKNOWLEDGEMENTS

This research work was supported by ScienceFund (03-01-02-SF0030) and Fundamental Research Grant Scheme (UKM-ST-06-FRGS0010-2007). The authors thank the staff of the Microscope Unit of Universiti Kebangsaan Malaysia for their assistance in obtaining the SEM and TEM images.

REFERENCES

- Alejandra, C.B.G., Luis, E.J. & Jose, Y.M. 2008. Characterization of low dimensional molybdenum sulfide nanostructures. *Materials Characterization* 59: 204-212.
- Baláz, P., Boldžarová, E., Godočíková, E. & Briančin, J. 2003. Mechanochemical route for sulphide nanoparticles preparation. *Material Letters* 57: 1585-1589.
- Hu, H., Bai, J., Guo, S. & Chen, G. 2002. Coal liquefaction with in situ impregnated Fe₂(MoS₄)₃ bimetallic catalyst. *Fuel* 81: 1521-1524.
- Kabil, M.A., Ghazy, S.E., El-Asmy A.A. & Sherif, Y.E. 1996. Highly selective procedure for trace analysis of platinum (IV) in its allied materials. *Analytical Sciences* 12: 431-437.
- Liao, X.H., Wang, H., Zhu, J.J. & Chen, H.Y. 2001. Preparation of Bi₂S₃ nanorods by microwave irradiation. *Materials Research Bulletin* 36: 2339-2346.
- Ma, L., Chen, W.-X., Li, H., Zheng, Y.-F. & Xu, Z.-D. 2008. Ionic liquid-assisted hydrothermal synthesis of MoS₂ microspheres. *Materials Letters* 62: 797-799.
- Monteiro, O.C., Nogueira, H.I.S., Trindade, T. & Motevalli, M. 2001. Use of dialkyldithiocarbamate complexes of bismuth(III) for the preparation of nano- and micro-sized Bi₂S₃ particles and the X-ray crystal structures of [Bi{S₂CN(CH₃)(C₆H₁₃)₃}] and [Bi{S₂CN(CH₃)(C₆H₁₃)₃}(C₁₂H₈N₂)]. *Chemistry of Material* 36: 2103-2111.
- Philias, J.M. & Marsan, B. 1999. FTIR spectroscopic study and thermal and electrical properties of polymer electrolytes containing a cesium thiolate/disulfide redox couple. *Electrochimica Acta* 44: 2351-2363.
- Philip, D., Eapen, A. & Aruldas, G. 1995. Vibrational and surface enhanced raman scattering spectra of sulfamic acid. *Journal of Solid State Chemistry* 116: 217-223.
- Qin, A.M., Fang, Y.P., Ou, H.D., Liu, H.Q. & Su, C.Y. 2005. Formation of various morphologies of covellite copper sulfide submicron crystals by a hydrothermal method without surfactant. *Crystal Growth Design* 5: 855-860.
- Subba, Reddy C.V., Walker, Jr E.H., Wen C. & Mho S.I. 2008. Hydrothermal synthesis of MoO₃ nanobelts utilizing poly(ethylene glycol). *Journal of Power Sources* 183: 330-333.
- Tian, D., Sharma, R.K., Stiller, A.H., Stinespring, C.D. & Dadyburjor, D.B. 1995. Direct liquefaction of coal using ferric-sulfide-based, mixed-metal catalysts containing Mg or Mo. *Fuel* 75: 751-758.
- Wang, H., Zhu, J.J., Zhu, J.M. & Chen, H.Y. 2002. Sonochemical method for the preparation of bismuth sulfide nanorods. *Journal of Physical Chemistry B* 106: 3848-3854.
- Zou, J., Zhang, J., Zhang, B., Zhao, P. & Huang, K. 2007. Low-temperature synthesis of copper sulfide nano-crystal of novel morphologies by hydrothermal process. *Material Letters* 61: 5029-5032.
- Fei-Ling Pua, Chin-Hua Chia, Sarani Zakaria*,
Tze-Khong Liew & Nay-Ming Huang
Pusat Pengajian Fizik Gunaan
Fakulti Sains dan Teknologi
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor
Malaysia
- Mohd Ambar Yarmo
Pusat Pengajian Sains Kimia dan Teknologi Makanan
Fakulti Sains dan Teknologi
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor
Malaysia

*Corresponding author; email: sarani@ukm.my

Received: 6 February 2009

Accepted: 25 August 2009